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AQUATIC ORGANISM ADHESION-PREVENTING MATERIAL AND PRODUCTION THEREOF

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AQUATIC ORGANISM ADHESION-PREVENTING MATERIAL AND PRODUCTION THEREOF

[Suiseiseibutsunofuchakuboshizairyo narabini sonoseizohoho]

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[There are no amendments to this patent.]

Claims

1. Aquatic organism adhesion-preventing material characterized by containing polyvinyl alcohol-coated repellent in coating components.

2. Aquatic organism adhesion-preventing material characterized by containing a mixture of polyvinyl alcohol and repellent in coating components.

3. Aquatic organism adhesion-preventing material characterized by containing polyvinyl alcohol-coated repellent which is further surface-modified with an oil component in the coating components.

4. A method for the manufacture of aquatic organisms [sic], characterized in that, in mixing and dispersing a repellent in coating components, the repellent is supported by polyvinyl alcohol then mixed and dispersed in coating components.

Detailed explanation of the invention

[0001]

Objectives of the invention

Industrial application field

The present invention concerns materials preventing aquatic organisms such as barnacles, hard-shelled mussels, etc. to ship bottoms, harbor facilities, crawls, etc.

[0002]

Background of the invention

To ships and various harbor facilities and fishing facilities such as fish nets, crawls, etc., exposed to seawater, barnacles, hard-shelled mussels, etc. adhere and live, resulting in reduced performance of such facilities and durability. Coating materials applied to ship bottoms for prevention of adhesion of such aquatic organisms have been developed. However, their effects for prevention of such aquatic organisms are not satisfactory. Moreover, many of such coating materials contain tin compounds, and the elution and diffusion of such compounds in surrounding sea and pollution of aquatic organisms is a problem.

[0003]

Given the current situation, we have developed various coating materials. However, workability in mixing and dispersing repellents into coating components, control of elution rate of repellents from coating surface, coating strength, etc. are not necessarily better than the conventional ones and require some improvements.

[0004]

Technology in development

With such background in mind, noting that by control of degree of polymerization and degree of saponification, solubility in cold water, aqueous solution viscosity, solvent resistance, film strength, etc. of polyvinyl alcohol can be controlled easily, development of materials

preventing aquatic organisms is tried by including a polyvinyl alcohol and repellent in the coating components of the present invention.

[0005]
Constitution of the invention
Means to achieve the objectives

Namely, the aquatic organism adhesion-preventing material in the first claim of this patent application is characterized by including polyvinyl alcohol-coated repellent in the coating components.

[0006]

The aquatic organism adhesion-preventing material in the second claim of this patent application is characterized by including a mixture of polyvinyl alcohol and repellent in the coating components.

[0007]

The aquatic organism adhesion-preventing material in the third claim of this patent application is characterized by including polyvinyl alcohol-coated repellent which is further surface-modified by an oil in the coating components.

[0008]

The method for the manufacture of aquatic organism adhesion-preventing material in the fourth claim of this patent application is characterized in that, in mixing and dispersing a repellent in coating components, the repellent is supported by polyvinyl alcohol then mixed and dispersed in coating components. The above objectives can be achieved by these inventions.

[0009]

Next, the present invention is explained in detail. First, the polyvinyl alcohol used in the present invention is explained. Of synthetic polymers, this polymer has a unique property, i.e., water solubility and is a powder with bulk density 0.2-0.7 and true density 1.27-1.31. This polymer has solubility in cold and hot water according to degree of saponification and is swelled or dissolved in acid or alkali.

[0010]

In terms of the mechanical properties of films, this polymer is excellent in tensile strength, tear strength, stretchability, wear resistance, etc., compared with other synthetic resins. This

polymer has excellent gas permeability, with exceptional permeation of steam. Due to the moisture absorption property, various physicochemical properties such as mechanical properties, electric properties, etc. vary greatly according to atmospheric temperature. Table 1 summarizes the relationship between general properties of polyvinyl alcohol with its degree of polymerization and degree of saponification.

[0011]

Table 1

	Degree of polymerization small → large	Degree of saponification small → large
Solubility in cold water	large ← small	large ← small
Solubility in hot water	large ← small	small → large
Aqueous solution viscosity	small → large increase	small → small increase
Film strength	small → large	small → large
Film elongation	large ← small	large ← small
Solvent resistance of film	small → large	small → large

[0012]

Next, the repellents included in the coating components are explained. The repellents have a physiological action on the aquatic organisms and can be applied in the form of liquid or powder as long as repellent effects are displayed. More specifically, recently recognized for repellent effects are eucalyptus oil (cineol, eucalyptol), tannin, tannic acid, saponin, etc.; sodium chloride, potassium chloride, magnesium sulfate, calcium chloride, etc. which are in sea water in high contents with repellent effects in sea water; wasabi, cayenne (extract powder), caffeine, etc. displaying repellent action by irritation or stimulation; enzymes such as lipase, amylase, protease, etc. displaying repellent effects by decomposition action of proteins, etc.; toxicants such as nicotine, nicotinic acid, etc.; healing materials such as aloe extract, propolis, etc.; Na salicylate, limonene, barium titanate, amino-modified silicone oil, zinc oxide-titanium dioxide-water bonded tight particles, etc. For example, saponin and copper chloride are mixed with an aqueous sodium chloride solution and dried to obtain a composite powder of such repellent materials.

[0013]

Next, the coating components that are used in the present invention may be those commonly used in coating materials for ship bottoms. Namely, they comprise a resin component, body pigments, color pigments, plasticizers, additives, etc. mixed in an appropriate ratio as

needed. Here, the resin component may be, e.g., chlorinated rubber, vinyl chloride, vinyl chloride-vinyl propionate, chlorinated polyolefins, acrylic resins, styrene-butadiene, rosin, rosin esters, rosin soaps, etc. The body pigment may be calcium carbonate, talc, silica, barium sulfate, clays, etc. The color pigment may be titanium white, rouge, etc. The plasticizer may be dioctyl phthalate, tricresyl phosphate, chlorinated paraffin, etc. Possible additives may be sedimentation preventers, sagging preventers, leveling agents, etc.

[0014]

Next, the method for making aquatic organism adhesion-preventing materials of the present invention is explained. In the case of repellent powders, repellent powder is mixed into a polyvinyl alcohol aqueous solution, then the repellent powder is removed and heat-dried to obtain repellent K whose surface is coated with polyvinyl alcohol P. This is then mixed and stirred with the coating component T for uniform dispersion to obtain an adhesion-preventing material shown in Figure 1(a). When two or more different types of polyvinyl alcohol-coated powder are dispersed in the coating component T, synergetic or complementary repellent effects may be obtained.

[0015]

Also, in the case of repellent powder, repellent powder K is mixed into a polyvinyl alcohol aqueous solution and dispersed into the coating components. In this case, as shown in Figure 1(b), droplets of polyvinyl alcohol P-coated repellent K and polyvinyl alcohol P are mixed in the coating component T.

[0016]

In the case of water-soluble repellents, an aqueous solution of repellent K is mixed with an aqueous solution of polyvinyl alcohol P, then the mixture is dried to obtain a powder which is then mixed with the coating component T to obtain polyvinyl alcohol P and repellent K independently dispersed in the coating component T as shown in Figure 1(c). Repellent K available only in a liquid or oil-soluble form may be mixed with a polyvinyl alcohol aqueous solution then dispersed in the coating component T.

[0017]

When polyvinyl alcohol-coated powdered repellent is to be mixed into coating components in the above preparation method, the repellent may be immersed into an oil component such as silicone oil, removed from the oil, dried and mixed and dispersed into coating components. The adhesion-preventing materials prepared with such a treatment have

water-repellent properties and lubricity by the action of silicone oil. Thus, such materials can be coated on ship bottoms. The water repellent property results in reduced probability of contact between sea water and repellent with suppression of elution of repellent in that proportion with sustained repelling effects of the adhesion-preventing material. On the other hand, beside the repelling action of the repellent, the lubricity also provides aquatic organism adhesion prevention effects by mechanical action.

[0018]

Function of the invention

In the present invention, in the coating components, the repellent is coated with polyvinyl alcohol or the repellent and polyvinyl alcohol are in a mixed state. Thus, when adhesion-preventing material is coated on ship bottoms, the polyvinyl alcohol is swollen by absorption of sea water, and the high concentration of repellent component enhances the aquatic organism repelling effects.

[0019]

When the repellent is coated with polyvinyl alcohol, elution of the repellent component present in high concentration at the polyvinyl alcohol is suppressed by the polyvinyl alcohol layer, resulting in gradual elution and dispersion of the repellent into sea water, thus providing sustained repellent effect by maintaining a high concentration region.

[0020]

By control of degree of polymerization and degree of saponification, cold water solubility, aqueous solution viscosity, solvent resistance, film strength, etc. of the polyvinyl alcohol can be easily designed. Therefore, if the repellent is supported by polyvinyl alcohol and mixed into coating components, solubility, elution speed and self-polishing speed can be easily controlled, and by control of viscosity, workability during coating material preparation and phase property with repellent can be easily controlled. Furthermore, by control of solvent resistance and film strength, phase property with coating solvent and film strength of the adhesion preventing material can also be easily controlled.

[0021]

The dispersion of polyvinyl alcohol-coated repellent surface-modified by oil component into the coating component enhances water repellency and lubricity of the repellent surface, resulting in improved durability of the repellent effect and adhesion prevention of aquatic organisms by mechanical action.

[0022]

Examples

Application Example 1

A mixture was prepared from 2 parts of 80-85% eucalyptus, product of Takasago Perfume Co. and 50 parts of 10% aqueous solution of polyvinyl alcohol GM-14, product of Nippon Gosei Kagaku Co., stirred, dried and pulverized, and 40 parts of this pulverizate was mixed and dispersed in 60 parts of acrylic resin to obtain coating material of Application Example 1. The acrylic resin was Acrydic A-198-XB, product of Dainippon Ink Kagaku Kogyo Co.

[0023]

Application Example 2

A mixture was prepared from 2 parts of α-amylase, product of Wako Junyaku Kogyo Co. and 50 parts of 10% aqueous solution of polyvinyl alcohol GL-500, product of Nippon Gosei Kagaku Co., stirred, dried and pulverized, and 40 parts of this pulverizate was mixed and dispersed in 60 parts of acrylic resin to obtain coating material of Application Example 2.

[0024]

For confirmation of adhesion prevention effects of each example, plate test and beaker test were carried out. First, in the plate test, as shown in Figure 2, on an acrylic FRP substrate (1) of a desired dimension, aquatic organism adhesion-preventing material M of the present invention was coated into a circle with diameter 5 cm, and near center, blue mussel with shell length 3 cm was fixed horizontally, and observation was made for the adhesion (on the table) position of bysal threads (a) from the blue mussel. Blue mussel is a typical aquatic organism used for adhesion tests along with barnacles, easily adheres to marine structures and is provides good objective data by simply counting number of byssal threads in table test. For such reasons, it is used for testing.

[0025]

More specifically, for fixing blue mussel A in this experiment, the blue mussel is directly bonded using an instantaneous adhesive, etc. via a rubber piece of about 1.2 mm thickness to the center part of the coated adhesion-preventing material M and placed in a sea water bath for about 1 week, and the state of bonding of byssal threads on the floor is observed. In evaluation, if the byssal threads go over the adhesion-preventing material M and extend to the outer acrylic FRP substrate (1), it clearly means that the byssal threads of blue mussel are repelled by the adhesion-prenventing material M. The larger the proportion (%) of the number of byssal threads reaching the outer area of the adhesion-preventing material to the number of grown byssal threads, the better the adhesion prevention effects.

[0026]

The beaker test is for enhanced precision of effect confirmation. In this test, as shown in Figure 3, entire inner surface of the beaker (2) of desired size, e.g., 300 cc is coated with the above adhesion preventing material M. After drying, the beaker is filled with about 280 cc of sea water, a blue mussel A is immersed in the beaker, allowed to stand for 1 week and inspected for any byssal threads adhered to the beaker inner wall (flooring). In the evaluation of adhesion prevention effect in this test, dead shell and no byssal thread growth indicate effectiveness, while growth of byssal threads sticking to the beaker bottom or sidewall with fixation of shell indicates lack of effectiveness. Each experiment is performed with 2 beakers.

[0027]

Effect of the invention

The results of each test are given in Table 2.

[0028]

Table 2

	Plate test	Beaker test
Application Example 1	No byssal threads from 4 bodies Adhesion of byssal threads on the plate from two bodies	Three dead One fixed to beaker side wall with byssal thread adhesion
Application Example 2	One dead Two with no byssal threads Three with adhesion of byssal thread on plate	All four dead

*In the table, the fractions indicate floored state of the byssal threads on the plate, and the denominators indicate the total number of floored byssal threads of blue mussel, and the numerators indicate the number of floored byssal threads extending to the outer side of the coated area of diameter 5 cm.

[0029]

As shown in Table 2, in Application Example 1, four showed no byssal threads at all, while two showed growth of byssal threads all of which adhered to outside of the coated area,

i.e., repellency 100%. In Application Example 2, one dead with two with no byssal threads at all. The other three had byssal threads, while two of the three had byssal threads adhered to outside of the coated area, and one the three had two byssal threads with only one adhered to the outside of the coated area. In the beaker test, there were three dead in Application Example 1, while one had its body fixed to the beaker sidewall with adhesion of byssal threads, and in Application Example 2, all four were dead.

[0030]

According to overall evaluation of such plate test and beaker test, it is apparent that the coating materials of Application Example 1 and Application Example 2 of the present invention have significant repelling effects against aquatic organisms.

[0031]

Furthermore, in the present invention, polyvinyl alcohol-coated repellents are included in coating components or repellents are included together with polyvinyl alcohol in the coating components, thus control of degree of polymerization and degree of saponfication of polyvinyl alcohol, free selection of repellents according to aquatic organisms to be repelled, and repelling action strength and durability can be designed as needed for application.

[0032]

Furthermore, composite coating materials capable of preventing adhesion of a number of aquatic organisms different in types of shells and water plants can be prepared, and polyvinyl alcohol does not adhere to proteins and adhesion prevention effect is expected against both animal and aquatic organisms.

Brief description of the figures

Figure 1 is an explanatory diagram with a schematic illustration of various examples of aquatic organism adhesion preventing materials that can be prepared by the method of the present invention.

Figure 2 is a perspective diagram illustrating a plate test which is a test method of the present invention for aquatic organism adhesion preventing materials.

Figure 3 a perspective diagram illustrating a beaker test which is a test method of the present invention for aquatic organism adhesion preventing materials.

Explanation of reference symbols

1 Acrylic FRP substrate

2 Beaker

A Blue mussel
a Byssal threads
K Repellent
M Adhesion-preventing material
P Polyvinyl alcohol
T Coating component

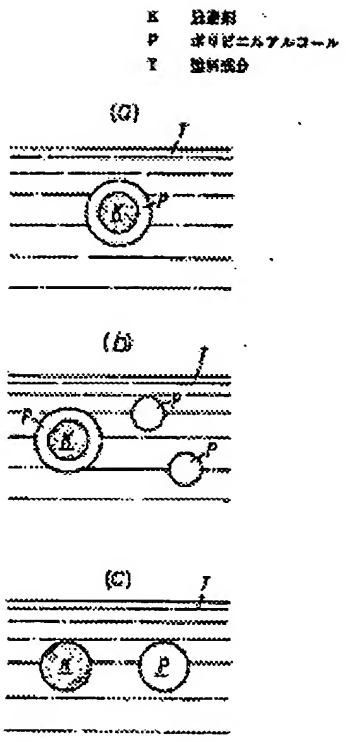

Figure 1

Legend: K: Repellent
P: Polyvinyl alcohol
T: Coating component

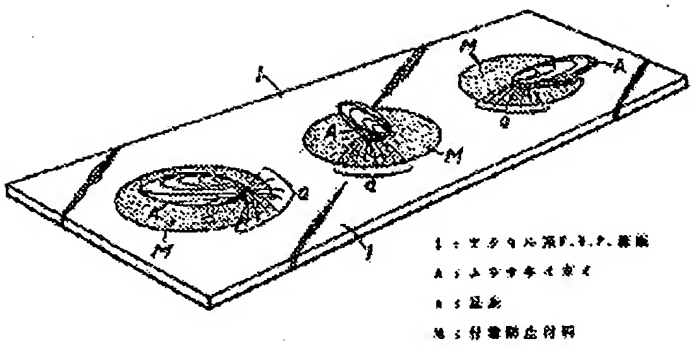

Figure 2

Legend:
1: Acrylic FRP substrate
A: Blue mussel
a: Byssal threads
M: Adhesion-preventing material

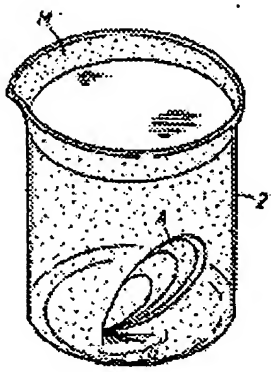

Figure 3